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博　士　学　位　论　文

典型多环芳烃在红树林沉积物中的吸附及其影响因素研究

Study on the sorption of typical PAHs in mangrove sediment and their influencing factors

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摘　要

多环芳烃（Polycyclic Aromatic Hydrocarbons，PAHs）是一类典型的持久性有机污染物，它可通过各种环境介质（大气、水、生物等）长距离迁移并存在于河口及海岸带生态环境中。红树林是热带、亚热带海岸重要的湿地生态系统，其生产力高、富含有机质以及强还原性环境条件等特性，使之成为吸收和累积 PAHs 的重要场所。但目前有关红树林湿地中 PAHs 的研究大多限于 PAHs 的含量及来源解析、微生物对 PAHs 的降解等。PAHs 在沉积物中的吸附行为及其影响因素的研究少见报道。红树林沉积物具有特殊性，且环境条件复杂多变，PAHs 在其中的吸附行为可能与其他沉积物不同。相关研究工作的开展对于红树林湿地的污染控制和生物修复有重要意义。

本文以三种典型 PAHs 萘（Na）、蒽（An）和苯并[a]芘（B[a]P）为代表，研究了它们在九龙江口红树林沉积物中的吸附行为及其受老化、淹水、温度、盐度和种植秋茄（*Kandelia candel*，*Kc*）幼苗的影响。另外，尝试将本课题组新建的荧光分析法应用于上述研究，以进一步拓展 PAHs 的现场、原位研究方法。主要研究内容和结果如下：

（1）新建了同步荧光法直接测定不同沉积物提取液中 Na、An 和 B[a]P 的方法。结果表明，该方法测定简单、快速，无需复杂前处理，其精确度和灵敏度可满足本研究的要求。

（2）研究了 Na、An 和 B[a]P 在沉积物中的吸附及其受老化和淹水作用的影响；分析了沉积物的组成和结构，探讨了 PAHs 吸附及老化、淹水作用的机理。结果表明，Na、An 和 B[a]P 在沉积物中的吸附依次增强；老化作用增强了 PAHs 在沉积物中的吸附，强吸附态 Na、An 和 B[a]P 分别由 48.6%、47.1%和 70.3%增至 50.5%，54.1%和 73.5%；淹水后，沉积物中约有 30.3%的 Na，16.8%的 An 和 3.46%的 B[a]P 释放至上覆水中，但老化后该释放量明显减少，分别为 18.4%，9.01%和 0.710%；所研究九龙江口红树林沉积物中主要的吸附剂是碳质颗粒和粘粒：碳质颗粒所占比重小，但吸附 PAHs 的量高；粘粒是该沉积物的重要组分，对沉积物富集 PAHs 贡献最大；该沉积物具有较好的团聚性。老化后，沉积物中的 PAHs 进入碳质颗粒和团聚体结构的微孔中，吸附于其中较深的吸附位点，较难被解吸。淹水作用在一定程度上破坏了沉积物团聚体的稳定性，从而使其吸附

的 PAHs 解吸。

（3）研究了 Na、An 和 B[a]P 在红树林沉积物上的吸附特性，以及温度和盐度对 PAHs 吸附的影响。结果表明，PAHs 在沉积物上的吸附均表现为快速吸附和慢速吸附两阶段过程；Freundlich 模型能很好地拟合等温吸附数据，由其拟合参数可知，沉积物对 PAHs 的吸附指数 n 全小于 1，表明吸附呈非线性；PAHs 的辛醇-水分配系数的对数（$\log K_{ow}$）与其在沉积物中吸附容量的对数（$\log K_f$）呈线性关系，表明吸附以分配作用为主；温度由 15 °C 升至 35 °C 时，PAHs 的吸附容量 K_f 明显减小，Na 的由 107.22 减至 10.792，An、B[a]P 的则分别从 246.22、2215.8 减至 33.524、491.13；盐度由 0 增至 30 时，PAHs 的吸附容量 K_f 增加，Na 的由 20.076 增至 215.46，An、B[a]P 的则分别从 73.029、1076.5 增至 361.10、2714.7。

（4）研究了 Na、An 和 B[a]P 在沉积物不同粒径团聚体中的吸附/解吸行为。结果表明，沉积物不同粒径团聚体对 PAHs 的吸附有明显差异。首先，其吸附动力学特征不同：在 0-2 h 快速吸附阶段，PAHs 的吸附速率和吸附量均随团聚体粒径减小而增加，在 2-72 h 的慢速吸附阶段，PAHs 的吸附速率和吸附量增率则随团聚体粒径减小而减小，快吸附阶段的差异与团聚体粒径有关，而慢吸附阶段的差异与团聚体结构有关；其次，其吸附容量 K_f 不同：不同粒径团聚体对 PAHs 的吸附容量 K_f 顺序为 0.063-0.25 > 0.063 > 0.25-1.0 > 1.0 mm，有机质的含量和性质是重要的影响因素。沉积物不同粒径团聚体中 PAHs 的解吸过程也表现为快速解吸和慢解吸两阶段，PAHs 在不同溶剂中的解吸量顺序为二氯甲烷 > 甲醇 > 羟丙基-β-环糊精（HPCD）水溶液，表明其吸附以疏水性分配为主；不同粒径团聚体中 PAHs 的解吸行为也表现出明显的差异；PAHs 在沉积物团聚体中的解吸与其吸附时间密切相关，吸附时间越长，解吸量越小。

（5）研究了种植典型红树植物 *Kc* 幼苗对沉积物中 Na、An 和 B[a]P 吸附行为的影响，及其受老化和淹水作用的影响。结果表明，种植 *Kc* 幼苗的沉积物中，Na、An 和 B[a]P 自然消解率分别为 55.05-71.54%、47.29-70.41%和 43.93-67.31%，明显高于未种植 *Kc* 幼苗的沉积物，表明种植 *Kc* 幼苗促进了沉积物中 PAHs 的自然消解；与未种植 *Kc* 幼苗的沉积物相比，种植 *Kc* 幼苗的沉积物中 HPCD 水溶液提取的 PAHs 和甲醇提取的 PAHs 含量较高，而剩余 PAHs 的含量较低，表明

种植 *Kc* 幼苗促进了沉积物中强吸附态 PAHs 向弱吸附态和生物可利用态转化；根际沉积物中生物可利用态 PAHs 的含量明显高于非根际沉积物；根际沉积物的酶活性明显高于非根际沉积物，表明根际环境中的微生物活性较高；沉积物中约 11.15-23.63%的 Na，3.81-5.65%的 An 和 0.32-1.18%的 B[a]P 被 *Kc* 幼苗根部富集，其中相当一部分被吸收至根内部。采用荧光显微镜法观察到了 An 向 *Kc* 幼苗茎、叶的传输；采用光纤荧光法在 *Kc* 叶片上下表面均检测到了 An，表明挥发再沉降也是 An 由沉积物向植物迁移的重要途径。三种 PAHs 在 *Kc* 幼苗根部的富集量与其在沉积物中的 HPCD 水溶液提取态含量有显著相关性，表明 *Kc* 幼苗根对三种 PAHs 的富集与其在沉积物中的吸附密切相关；老化后，三种 PAHs 在沉积物中的吸附增强，从而使其根富集量减小；淹水后，三种 PAHs 在沉积物中的吸附减弱，从而使其根富集量增加。

（6）综合上述结果可知，与其他沉积物相比，由于红树林沉积物本身性质及所处环境的特殊性，PAHs 在其中的吸附行为也表现出特殊性：红树林沉积物含有吸附能力强的碳质颗粒等有机吸附剂和粘粒含量高的特点使其易富集 PAHs；团聚结构好的特点使 PAHs 易被“扣押”而难于解吸；PAHs 吸附明显受老化、淹水、温度、盐度和红树植物的影响。

本研究结果为进一步揭示 PAHs 在红树林生态系统中的迁移转化规律提供研究信息，为红树林湿地的污染控制和植物修复提供重要的科学依据，也为更好地保护和利用红树林资源提供科技支撑，具有重要的科学意义和环境效益。

关键词： 多环芳烃；红树林；沉积物；吸附；红树植物

Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are an important class of persistent organic pollutants. They migrated long distances and stored in the estuaries and coastal environment through various environmental media (air, water, biological etc.). The mangrove ecosystem is an important intertidal estuarine wetland along tropical and subtropical coastlines. The unique features of mangroves such as high primary productivity, rich organic carbon and anoxic conditions make them an ideal 'sink' for uptake and preservation of PAHs. The published research on PAHs in the mangrove wetland has mainly focused on the concentrations and sources of PAHs and the degradation of PAHs by microorganisms. Research on the sorption of PAHs in mangrove sediments is rarely carried out. Mangrove sediment with its own characters, when suffered from complex environmental conditions, their sorption behaviors may be different from other sediments. The involved research will be important for pollution controlling and bioremediation of pollutants in mangrove wetland system.

In this study, the sorption behaviors of three typical PAHs, naphthalene (Na), anthracene (An) and benzo[a]pyrene (B[a]P) in the sediment from Jiulong river estuary mangrove, and the effects of aging, flooding, temperature, salinity and planting *Kandelia candel* (*Kc*) seedings on those behaviors were studied. Furthermore, the newly established fluorescence methods were introduced in this study, thus to develop the in-situ research methods on the study of environmental behaviors of PAHs in mangroves. Research contents and results in this study are as follows:

(1) A novel synchronous fluorescence spectrometry (SFS) method for the direct determination of Na, An, and B[a]P in different sediment extracts was established. The results showed that the method was not only simple and rapid, but also needed no complicated pretreatments and both of precision and sensitivity meet the requirement for the study.

(2) The sorption fractions of the PAHs in mangrove sediment and the effects of aging and flooding on the PAHs sorption were studied. The relative mechanisms were also discussed by the analysis of sediment compositions and structures. The results

showed that the sorption of Na, An and B[a]P in the sediment were increased in turn. After aging, the sorption of the PAHs in sediment were increased, such as, the strongly sorbed fractions of Na, An and B[a] P increased from 48.6%, 47.1% and 70.3% to 50.5%, 54.1% and 73.5%. After flooding, 30.3%, 16.8% and 3.46% of Na, An and B[a]P were released from sediment to cover water, but the release rations were decrease to 18.4%, 9.01% and 0.710% after aging. The main adsorbents of the studied mangrove sediment in Jiulong river estuary are carbon particles and clays. Although the proportion of carbon particles was small, they adsorbed relatively high amount of PAHs; clays are important components of mangrove sediments and are significant for the sorption of PAHs in sediment. The aggregates which are the combinations of clay minerals can fixe PAHs, but after flooding, the structural stability of the aggregates was destroyed in some extent, and then induced the release of PAHs in sediment. The sediment had stable aggregates. PAHs entered into the micropores of carbon particles and sediment aggregates with aging, and then absorbed on deeper absorption sites, so that they were difficult to be desorbed. The stability of sediment aggregates was destroyed by flooding, so that the PAHs in sediment aggregates were released.

(3) The sorption characters of Na, An, and B[a]P in mangrove sediment and the effects of temperature and salinity on the sorption characters were studied. The results demonstrated that the sorption of the PAHs in the mangrove sediment were two-step processes, including a rapid sorption process and then a slow sorption process. The sorption process can be well described by Freundlich model, and the sorption of the PAHs on sediment was nonlinearity. The $\log K_f$ of the PAHs in sediment and their $\log K_{ow}$ have linear correlation, indicating that the main process of the sorption of the PAHs in sediments was partitioning. As the temperature increased from 15 °C to 35 °C, the K_f values of Na, An and B[a]P were decreased from 107.2, 246.2 and 2216 to 10.79, 33.52 and 491.1, respectively. As the salinity increased from 0 to 30, the K_f values of Na, An and B[a]P were increased from 20.076, 73.029 and 1076.5 to 215.46, 361.10 and 2714.7, respectively.

(4) The sorption and desorption behaviors of the PAHs in sediment aggregates with different sizes were studied. The results showed that the sorption kinetics of the

PAHs in different size aggregates differed from each other. With the decrease of the size of aggregates, the rates and amounts of the sorption of PAHs in sediment were increased at 0-2 h rapid sorption step, but decreased at 2-72 h slow sorption step. The difference of the rapid sorption step was due to the size of aggregates, while the difference of the slow sorption step was due to the structure of aggregates. The sorption contents K_f of PAHs in different size aggregates followed the order of, 0.063-0.25 mm > 0.063 mm > 0.25-1.0 mm > 1.0 mm, and the differences were due to the contents and characters of organic matters in aggregates. The desorption behaviors of PAHs in sediment aggregates were two-steps, with a short period of rapid desorption at first and followed by a long-time slow desorption. The extraction efficiencies of the PAHs in sediment by different extraction solvents were in the order of, dichloromethane (DCM) > methanol > hydroxypropyl-β-cyclodextrin (HPCD), which indicated that hydrophobic partitioning played a dominant role in PAHs sorption. The desorption behaviors of the PAHs in different size aggregates were also different. With the increment of sorption times, the amounts of desorption equilibrium of the PAHs in aggregates decreased.

(5) The effects of planting *Kc* seedings on the sorption of the PAHs in mangrove sediment, and the effects of aging and flooding were investigated. The results showed that the removal percentages of Na (55.05-71.54%), An (47.29-70.41%), and B[a]P (43.93-67.31%) in mangrove planted sediments were higher than those of non-planted sediments. The HPCD and methanol extracted PAHs of planted sediments were higher than those of non-planted sediments, while the DCM extracted PAHs of planted sediments were lower than those of non-planted sediments, indicating that planting *Kc* seedings strongly promoted the PAHs transferring from strongly sorbed fraction to weakly sorbed and bioavailable fractions in sediments. The bioavailable PAHs of rhizosphere sediments were significantly higher than those of non-rhizosphere sediments. The sucrase and urease activities of rhizosphere sediments were significantly higher than those of non-rhizosphere sediments, indicating that microbial activity of rhizosphere sediment was higher, which can be used to explain why the bioavailable PAHs of rhizosphere sediments were higher than those of

non-rhizosphere sediments. About 11.15-23.63% of Na, 3.81-5.65% of An and 0.32-1.18% of B[a]P in planted sediments were accumulated by *Kc* seedings roots. The results of sequential extraction for the PAHs in plant roots showed that a part of PAHs were existed in root tissues. The transportation of the PAHs from root to stems and leaves was investigated by fluorescence microscopy, indicating that the PAHs in sediments could transport from mangrove roots to up-ground tissues. The fluorescence signal of PAHs were detected both in the upper and lower surfaces of mangrove leaves by fiber-optic fluorimetry, suggesting that the volatilization and resettlement of the PAHs form sediment to leaf surface took place, which was another migration approach of the PAHs from sediment to mangrove plant. PAHs accumulated in *Kc* seedings roots were correlated with the HPCD extracted PAHs in sediments, which indicated that the accumulation of PAHs by *Kc* seedings roots was correlated with the sorption of PAHs in sediment. Aging strengthened the sorption of PAHs in sediment, and then decreased PAHs accumulated by plant roots. Under flooding cultivation, the extractability of PAHs in sediments increased and then the root uptake of PAHs were increased.

(6) From the above results, it can be seen that, the sorption behaviors of PAHs in mangrove sediment were different from another sediments due to its own characters and the special environmental conditons: Carbon particles and clays existing in mangrove sediments can absorb PAHs, sediment aggregates can sequestrate PAHs and make them difficult to be desorbed, and the sorption behaviors of PAHs in mangrove sediment were influened by aging, flooding, temperature, salinity and planting *Kandelia candel* (*Kc*) seedings.

This research provide valuable informations for the further study on the transformation of PAHs in mangrove wetland, a scientific basis for the environmental risk assessment, pollution control and phytoremediation of mangrove wetlands, and also a scientific and technological support for the protection of mangrove resources which have both significant scientific meaning and environmental benefits.

Key Words: PAHs; mangrove; sediment; sorption; mangrove plant

目　录

Contents